

TITLE OF THE INVENTION

MOISTURE ACTIVATED SINGLE-COMPONENT EBONITE COMPOSITION

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INVENTORS

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from a provisional patent application No. 60/443,125, filed 01/27/2003, the content of which is incorporated herein by reference.

FIELD OF THE INVENTION

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This invention relates generally to ebonite compositions useful for protecting metals from corrosion and chemical attack. More particularly, it relates to a single-component moisture activated liquid ebonite coating that does not require premixing and does not sag or run off.

DESCRIPTION OF THE BACKGROUND ART

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Ebonite or hard-rubber linings have been used for decades for protecting metals from corrosion or chemical attack as documented in "Corrosion Prevention by Protective Coatings, Second Edition, Chapter 20," by Charles Munger, 1999 (Publisher: National Association of Corrosion Engineers). Such linings are applied in sheets and require adhesive bonding to the metal surface as well as at the overlays. The application is craft sensitive and time consuming.

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To overcome the disadvantages of the ebonite or hard-rubber linings, several single-component liquid rubber based ebonite coatings have also been disclosed by Rappoport in U.S. Pat. No. 5,766,687 and U.S. Pat. No. 5,997,953, by Figovsky in WO 0,006,639, and by Petrovic *et al.* in DE 3,740,181. These liquid coatings can be rolled, brushed, trowelled or sprayed onto the metal surface to form a monolithic layer, thus simplifying the application.

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However, these single component ebonite coatings still suffer from two major drawbacks. First, they will sag, drip, flow or run off on a non-horizontal surface when subjected to the subsequent heating during the vulcanization stage and result in uneven coating, which compromises its protective function. Second, their surface is tacky, making it difficult for
5 multiple coats.

To overcome the run-off problem and to achieve a tack free surface to facilitate handling, Chang *et al.* in U.S. Pat. No. 6,482,894 disclosed a two-component liquid ebonite coating system. The second component is based on an unsaturated liquid rubber which contains a
10 functional group capable of reacting with the functional group in the first component at room temperature. When the two components are mixed and applied, e.g. by spraying, onto a metal substrate, the coating will gel at the room temperature and thus prevents run-off during the subsequent vulcanization stage. Hoelter *et al.* in U.S. Pat. Application 2002/0002244 also proposed a two component coating system, with the second component being mainly low
15 molecular weight polyisocyanates. Although the two-component liquid ebonite coatings solved the run-off problem, the two component coating system of Hoelter *et al.* requires an extra step of mixing the two components before application onto the metal substrate.

To overcome the shortcomings of aforementioned various linings and coatings, the present
20 invention discloses a single-component moisture activated liquid ebonite coating that does not require premixing and does not sag or run off.

SUMMARY OF THE INVENTION

We have discovered that a single component sag-free liquid ebonite coating can be realized
25 by judicious selection and addition of silane coupling agents to the ebonite mixture. The present invention provides a single component moisture activated liquid ebonite composition that is particularly useful for coating applications in protecting metal from corrosion and chemical attack. In some embodiments, the single component moisture activated liquid ebonite composition having a total mass percentage of 100 is comprised of:

- 30 liquid unsaturated rubber of about 15-85 mass percentage;
- sulfur of about 10-50 mass percentage;

a vulcanization activator, such as zinc oxide, magnesium oxide, or their metallic salts, of about 5-35 mass percentage;

a vulcanization accelerator of about 0.2-2.0 mass percentage;

carbon black of about 1-10 mass percentage;

5 a first silane of about 5-10 mass percentage, the first silane is particularly selected such that it can chemically bond to the liquid unsaturated rubber while leaving the alkoxy groups thereof intact, thereby converting the liquid unsaturated rubber to alkoxy functionality at the end of the treatment with the first silane;

a second silane of about 1-10 mass percentage, the second silane consuming and
10 scavenging moisture originally present in the mixture, substantially increasing the shelf stability of the mixture, the second silane is substantially non-reactive during the treatment with the first silane;

a third silane of about 1-10 mass percentage, the third silane containing sulfur linkages and reacting with the sulfur during vulcanization, the third silane can be selected
15 with the right reactive functional group to replace the first silane or the second silane;

an optional catalyst of about 0.01-2 mass percentage, the catalyst promoting and accelerating reaction of the liquid unsaturated rubber and the first silane;

a filler of about 0-60 mass percentage;

optional additives of about 0-10 mass percentage; and

20 an optional diluent or solvent of about 0-30 mass percentage can be added to control viscosity of the mixture.

The composition exhibits adequate shelf stability without pre-gelling during storage and shipping. The coatings can be applied by a single component spray equipment onto a metal
25 substrate, the moisture in the ambient will activate silane coupling agent(s) and gel the coating, which prevents sagging, dripping or run-off. The coatings also become tack free within 24 hours, making it possible for inspection as well as facilitating multiple coats when necessary. The single component sag-free liquid ebonite coatings thus greatly simplify the manufacturing, handling, shipping and application processes. After the coatings are subjected
30 to a subsequent vulcanization at elevated temperatures, they develop excellent physical and

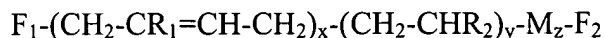
adhesion properties. The coatings are particularly useful for protecting a metal substrate from corrosion and chemical attack.

DESCRIPTION OF THE INVENTION

- 5 According to the present invention, the single component sag-free liquid ebonite coating composition consists of the following ingredients and their mass percentages. The total mass percentage of all ingredients must be 100%.

	Mass %
1. Liquid unsaturated rubber	15- 85
2. Sulfur	10- 50
3. Zinc Oxide or Magnesium oxide	5- 35
4. Vulcanization accelerator	0.2-2.0
5. Carbon black	1- 10
6. First silane capable of chemical bonding to 1	5-10
7 Second silane as moisture scavenger	1-10
8. Third silane capable of reacting with sulfur during vulcanization	1-10
9. Catalyst that promotes reaction of 1 and 6	0.01-2
10. Filler	0-60
12. Other additives	0-10
13. Diluent or solvent	0-30
Total	100%

- 10 The liquid unsaturated rubber has the general formula of:



Where $R_1 = H$ or CH_3

- 15 $R_2 = H, CH_3, C_2H_5, \text{phenyl, nitrile, acrylate, acetate, etc.}$

$F_1 = \text{H, CH}_3, \text{OH, COOH, NH}_2, \text{NCO, epoxy, vinyl, acrylate, anhydride, etc.}$

$F_2 = \text{H, CH}_3, \text{OH, COOH, NH}_2, \text{NCO, epoxy, vinyl, acrylate, anhydride, etc.}$

F_1 and F_2 can be the same or different.

M is the third monomer, which can be noborene, hexadiene or cyclopentadiene, etc.

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When F_1 and F_2 are either H or CH_3 , the liquid rubber is called non-functional. The liquid rubber can be linear which contains two chain ends, or branched which contains more than two chain ends or functional groups. The liquid rubber can also be partially epoxidized or maleinized through its double bonds.

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Preferably, $5 < x+y+z < 150$ so that the molecule is liquid at ambient temperature. The molecular mass of the liquid rubber can be from 200 to 10,000, preferably from 1,000 to 8000, and most preferably from 2,500 to 6,000. Also, it is preferable that $x / (x+y+z) > 0.4$ so that there are sufficient double bonds for sulfur vulcanization, and this is true even if the

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liquid rubber is partially epoxidized or maleinized.

The composition can contain a mixture of liquid rubbers that have different molecular mass or functional groups so long as they do not react under ambient condition.

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Some commercial liquid rubber include hydroxyl terminated polybutadiene Polybd 45HTLO and Polybd R-20 LM from Atofina, Liquiflex H and Liquiflex P from Petroflex, Krasol LBH from Kaucuk, isocyanate terminated polybutadiene Krasol LBD, Krasol NN, and Krasol NH from Kaucuk, maleinized polybutadiene Krasol LBM from Kaucuk, Ricon MA from Ricon Chemicals, epoxidized polybutadiene Polybd 600E and Polybd 605E from Atofina,

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nonfunctional polybutadiene Krasol LB, Krasol PS, Krasol PP from Kaucuk, Ricon from Ricon Chemicals, isolene polyisoprene and DPR liquid natural rubber from Elementis, Ricon copolymer for butadiene and styrene from Ricon Chemicals, acrylic terminated polybutadiene Ricacryl from Ricon Chemicals, etc.

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Sulfur can be rubber makers sulfur such as Redball Superfine supplied by International Sulfur or insoluble sulfur such as Crystex supplied by Flexsys, or their equivalents.

Optionally, a portion of the sulfur can be replaced by an organic sulfur donor compound such as Sulfasan DTDM supplied by Harwick Chemicals, or its equivalents.

5 Zinc oxide is commonly used as activator during sulfur vulcanization reaction with unsaturated rubber. Magnesium oxide or other metal oxides are sometimes used. The metal oxides can be totally or partially replaced with their metallic salts such as zinc stearate, etc.

Accelerators speed up the sulfur vulcanization reaction and allow the reaction to complete either at a lower temperature or in a shorter time. Commonly used accelerators include
10 thiurams such as tetramethylthiuram disulfide, tetrabutylthiuram disulfide, tetraisobutylthiuram disulfide, tetrabenzylthiuram disulfide, tetraalkylthiuram disulfide, 2-mercaptobenzothiazole, benzothiazyl disulfide, N-oxydiethylenebenzothiazole-2-sulfenamide, N-cyclohexyl- benzothiazole-2-sulfenamide, N-tert-butyl-2-benzothiazolesulfenamide, diphenylguanidiene, N,N'-ditolylguanidiene, aldehyde-aniline
15 condensation products, bismuth dimethyldithiocarbamate, cadmium dimethyldithiocarbamate, cadmium diethyldithiocarbamate, copper dimethyldithiocarbamate, lead dimethyldithiocarbamate, selenium dimethyldithiocarbamate, selenium diethyldithiocarbamate, Tellurium dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc diethyldithiocarbamate, zinc di-n-butylthiocarbamate, zinc diamylthiocarbamate,
20 thiodiazine, diethylthiourea, trimethylthiourea, dibutylthiourea, zinc isopropyl xanthate, etc.

Carbon black is used for color, enforcement or to impart thermal or electrical conductivity to the ebonite vulcanizates.

25 The general formula for silanes is $R_nSiX_{(4-n)}$, where Si is a silicon atom, R is an alkyl radical containing a reactive functional group and X is an alkoxy group, most commonly methoxy, ethoxy or butoxy groups, and n is between 1 to 3. The reactive functional group of the first silane is so selected that will chemically bond to the unsaturated liquid rubber while leaving alkoxy groups intact. For example, if a hydroxyl terminated liquid rubber is chosen, an
30 isocyanate or anhydride functional silane can be employed. If an epoxidized liquid rubber is chosen, an amine functional silane can be used. If an isocyanate functional liquid rubber is

chosen, either a hydroxyl, or amine functional silane can be used. If a non-functional liquid rubber is chosen, an acryl functional silane is selected. With peroxide or UV, the acrylic group can bond to the double bonds of the unsaturated liquid rubber. At the end of the first silane treatment, the liquid rubber is converted to alkoxy functionality. It is important that
5 during the silane treatment and in the subsequent storage, moisture should be kept out or minimized so that the water molecules in the ambient will not react to alkoxy groups prematurely.

A second silane is added to work as a moisture scavenger. It is quite common that any raw
10 materials in the formulation could contain a small amount of adsorbed or absorbed water. The second silane is added to consume, through its alkoxy groups, water that are originally present in the formulation. The functional group on the second silane is substantially non-reactive during the treatment with the first silane. The addition of the second silane can greatly increase the shelf stability of the mixtures.

15 Also, a third silane containing sulfur linkages can be added. Such sulfur containing silane has the general formula of $R_nX_{(3-n)}Si-S_m-SiX_{(3-n)}R_n$, where Si, R and X are the same as previously defined and n is between 0 to 2 and m is between 2 to 8. The sulfur linkage allows the third silane to be incorporated into the sulfur-rubber networks during the vulcanization reaction
20 and render better physical properties. The third silane, if it has the right reactive functional group, can be used to replace the first silane to react with the functional group of liquid rubber to impart alkoxy groups, or it can be used to replace the second silane as moisture scavenger.

25 In the treatment of liquid rubber with the first silane, a catalyst may be added to accelerate the chemical reaction. For example, if a hydroxyl terminated liquid rubber is selected and a silane with isocyanate function group is used, a catalyst such as DABCO T12 (dibutyl tin dilaurate) can be used to speed up the reaction. Those skilled in the art will have no problem in selecting a proper catalyst depending on the functional group on the liquid rubber and that
30 of the first silane.

There are a variety of pigments or fillers that can be added to the mixture: fly ash, pumice, calcium carbonate, titanium dioxide, precipitated silica, fused silica, quartz, silicates, barium sulfide, talc, aluminum oxide, clay, iron oxide, micaceous iron oxide, glass flake, zinc sulfide, feldspar, wallastonite, mica, grounded rubber particles, zinc borate, etc.

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There are also additives that can be incorporated into the mixture including thixotropic agents, deaerating agents, defoaming agents, leveling agents, adhesion promoters, surfactants, dispersing agents, anti-settling agents, fungicides, corrosion inhibitors, colorants, etc. Optionally, some inorganic moisture scavenger such as zeolites can also be added.

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To control viscosity, sometimes a diluent or solvent can be added to facilitate spray or other type of applications.

The following are some working examples:

	Ingredient	Exp 1	Exp 2	Exp 3
Polybd 45HTLO	Hydroxyl terminated liquid butadiene (AtoFina)	46.26	46.27	46.26
Redball Superfine	Sulfur (International Sulfur)	23.12	23.13	23.12
Kadox 930	Zinc oxide (Zinc Corporation of America)	16.18	16.19	16.18
Mogul L	Carbon black (Cabot)	0.93	0.93	0.93
Silquest A-link 35	Isocyanate functional silane (OSi Crompton)	8.56	8.56	8.56
Silquest A 171	Vinyltrimethoxysilane (OSi Crompton)	1.74		
Silquest A 189	Mercaptotrimethoxysilane (OSi Crompton)		1.74	
Silquest A1289	Bis-(triethoxysilylpropyl)-Tetrasulfide (OSi Crompton)			1.74

Aerosil R972	Fumed silica (Degussa)	1.24	1.24	1.24
Dabco T12	Catalyst (Air Products)	0.12	0.09	0.12
Royalac 150	Tetraalkylthiuram disulfide (Uniroyal Chemicals)	1.85	1.85	1.85

First, Polybd 45HTLO, Redball Superfine, Kadox 930, Mogul L are hand mixed to wet the powders. The mixture was then stirred using a laboratory high-speed disperser at 2500 rpm for about 10 minutes to achieve homogeneous dispersion. Silanes and Royalac 150 were next
5 added while keep stirring at the same speed for one minute. The speed was reduced to 500 rpm and Aerosil R972 was added until it was well dispersed and the mixture became homogenous. Dabco T12 was added after the mixture cooled down to room temperature. After 24 hours, the isocyanate functional group of Silquest A-link 35 reacted with the hydroxyl groups of Polybd 45HTLO and the liquid rubber was converted to having
10 alkoxysilane functionality.

To ensure the shelf stability, the final mixture was sealed in a one-quart metal can and placed in a 70°C oven for three days. The mixture remained fluid without a significant increase in viscosity, so it had adequate shelf stability.

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To test the sag resistance and tack free time, a standardized steel panel (Q-Panel) was coated with the mixture by using a doctor blade to obtain a 10-mil coating thickness, and placed in a vertical position for 24 hours to check sagging according to ASTM D4400. During the same period, the coating was activated by the ambient moisture (relative humidity was 38 - 45%)
20 and started gelling. The tack free time was determined according to ASTM D2377-84.

To test the physical properties of the coatings, a 20-mil coating was applied onto a Q-Panel by a doctor blade. The coated Q-Panel was then placed in an air-circulated oven. The oven temperature was programmed to rise from 23°C to 180°C at the rate of 0.9°C per minutes.
25 The temperature was maintained at 180°C for one hour to fully vulcanize the coating. The

Shore D hardness, Pencil Hardness and Impact Resistance were tested according to the ASTM test methods.

To determine the adhesion strength to the steel surface, a 20 mil coating was applied onto a 1/8" carbon steel, the surface of which has previously been sand-blasted to white metal according to the NACE Standard #2. The coating was then vulcanized using the same temperature profile described in the previous paragraph. After the coating was cooled down to 23°C, the adhesion strength was determined by ASTM D4541.

All test results are summarized in TABLE I below.

TABLE I.

Property	Test Method	Exp 1	Exp 2	Exp 3
Shelf Stability	72 Hours @70°C	Pass	Pass	Pass
Sag Resistance	ASTM D4400	No Sag	No Sag	No Sag
Tack Free Time	ASTM D2377	24 hours	16 hours	18 hours
Shore D Hardness	ASTM D2240	87	86	86
Pencil Hardness	ASTM D3363	HB	HB	HB
Impact Resistance	ASTM D2794			
Front		48 lb-in	56 lb-in	20 lb-in
Back		4 lb-in	56 lb-in	4 lb-in
Adhesion (psi)	ASTM D4541	1700	1500	1550

Although the present invention and its advantages have been described in detail, it should be understood that the present invention is not limited to or defined by what is shown or discussed herein. The drawings, description and discussion herein illustrate technologies related to the invention, show examples of the invention and provide examples of using the invention. Known methods, procedures, systems, elements or components may be discussed without giving details, so to avoid obscuring the principles of the invention. One skilled in

the art will realize that implementations of the present invention could be made without departing from the principles, spirit or legal scope of the present invention. Accordingly, the scope of the present invention should be determined by the following claims and their legal equivalents.

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